

Patchy colloidosomes – an emerging class of structures*

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Abstract. A colloidosome, i.e., a selectively permeable capsule composed of colloidal particles forming a stable homogenous shell, is a tiny container that can be used for storage, transportation, and release of cargo species. There are many routes to preparing colloidosomes; dozens of examples of future applications of such colloidal capsules have been demonstrated. Their functionality can be further extended if the capsules are designed to have heterogeneous shells, i.e., one or more regions (patches) of a shell are composed of material with specific properties that differ from the rest of the shell. Such patchy colloidosomes, supplemented by functionalities similar to that offered by well-studied patchy particles, will surely possess advantageous properties when compared with their homogenous counterparts. For example, owing to specific interactions between patches, they either can self-assemble into complex structures; specifically adhere to a surface; release their cargo species in specific direction; or guided-align,–orient or –propel. Fabrication of patchy colloidal microcapsules has long been theorized by scientists able to design different models, but actual large-scale production remains a challenge. Until now, only a few methods for fabricating patchy colloidosomes have been demonstrated, and these include production by means of microfluidics and mechanical pipetting. The field of science related to fabrication and application of patchy colloidosomes is clearly unexplored, and we envision it blooming in the coming years.

1 Introduction

Microcapsules– tiny containers used for storage, transportation, and cargo species release–form a shell that can be made of different synthetic and natural materials, including thermo-responsive microgels formed from a network of polymers [1–3],

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pH-responsive polymer macromolecules [4,5], redox-responsive polymer macromolecules [6,7], block copolymers [8,9], proteins [10,11], or colloidal particles [12,13]. The microcapsules with shells made of colloidal particles are often called colloidosomes. These are fabricated by various methods that typically involve the formation of a Pickering emulsion [12–14], i.e., an emulsion with droplets solely stabilized by packed colloidal particles strongly adsorbed at the surface of a droplet [15–17]. Several types of nano- and microparticles were used as the building blocks of the shell, such as polystyrene spheres [18], magnetic iron oxide rods [19], plate-like anionic clay particles [20], or silica particles [13], and these allowed designing colloidosomes for a specific application. Colloidosomes are typically made of a monolayered shell, though fabricating a multilayered shell has also been demonstrated [21]. The colloidosome's shell has to be reinforced (usually done as the last step of the preparation), and this is achieved by the sintering of surface particles [22,23], gel trapping [24,25], covalent cross-linking of colloidal particles [26,27], or polymerization of a thin layer on the inner or outer side of the shell [28,29]. The supporting material often has an additional function: the mechanism of release or uptake is controlled via permeability changes in the material that fills up the pores between the colloidal particles.

In the last decade, a field of research related to the fabrication and usage of colloidosomes has rapidly grown. In spite of the many developments in colloidosome fabrication, this field of science has not yet reached the saturation level. In fact, this branch of research is about to bloom, especially if one takes into consideration that the functionality of colloidosomes (and also other types of capsules) can be further extended if the capsules have heterogeneous shells, where one or more regions (patches) of a shell are composed of material with properties that differ from the rest of the shell. Such patchy colloidosomes, supplemented by functionalities similar to those offered by well-studied patchy particles [30–34], will surely possess advantageous properties when compared with their homogenous counterparts. For example, owing to specific interactions between patches, they can self-assemble into complex structures; specifically adhere to a surface; release their cargo species in a specific direction; or guided-align,–orient or –propel (as discussed in the following sections). Scientists have long theorized about fabricating patchy colloidal microcapsules and have designed different models, but actual large-scale production remains a challenge. Until now, anisotropic (patterned) microcapsules have not often appeared in the literature. Only a few methods for fabricating patchy colloidosomes have been demonstrated, and these employ phase separation by dewetting, which occurs while drying Pickering droplets, or magnetic-field-induced asymmetric assembly of particles in Pickering droplets. In both cases the Pickering droplets are formed via double emulsification [35]; fluid-flow-assisted adsorption and packing of colloidal particles at gas–liquid or liquid–liquid interface in a hydrodynamic-focusing microfluidic device [36]; the electrocoalescing of droplets formed by using a mechanical pipette [37,38]; or chemical synthesis in an autoclave where shells are made by self-assembling at the gas–liquid interphase on growing gas bladders [39]. There is also an interest in researching other types of capsules and a few examples of patchy structures have been recently produced, including patchy polymersomes [40,41], patchy hybrid vesicles [42], and patchy microcapsules made of polyelectrolyte macromolecules [43]. Schematic representations of different patchy structures are presented in Fig. 1. In this mini-review article, we present examples of patchy colloidal capsules and discuss their advantages over the homogenous colloidal capsules. We also identify some of the current technical problems in fabricating such capsules and suggest directions for further investigation.

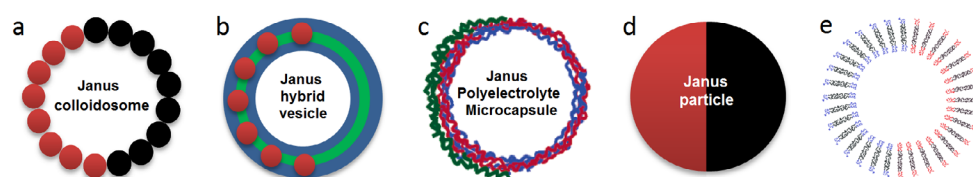


Fig. 1. Schematic representation of different types of patchy structures: Cross-sectional view of a Janus colloidosome (a); a Janus vesicle-nanoparticle hybrid (b); a Janus microcapsule made of polyelectrolyte macromolecules (c); a Janus particle (d); and a Janus polymersome (e).

2 Release of encapsulated species (homogeneous vs. patchy capsules)

Whether a capsule uses a fast or sustained release of encapsulated species determines its application range. Two types of mechanisms trigger the release from a capsule: an internal stimulus (e.g., changes of pH [4] or ionic strength of the solution [44]) or an external stimulus (e.g., light [46], magnetic or electric field [47,48], or ultrasound irradiation [49]). The microcapsule response may be based on either the intrinsic properties of the shell or the content of the capsule, and it is sensitive to the trigger impact [50,51]. The release can be achieved by irreversible shell decomposition (e.g., by melting, degradation, cracking, etc. [48]) or by a reversible change of the shell's permeability (e.g., by swelling [18]). In the following section, we will present in greater detail a few examples of pH-responsive homogenous capsules and juxtapose them with conceptual examples of heterogeneous colloidal capsules.

The pH-responsive capsules can be produced by different techniques, including microfluidics [4] and emulsification methods [18]. There are various mechanisms proposed to release an encapsulated material; and parameters, such as trigger pH value, time of release or release rate, can be adjusted by choosing adequate materials for the shell. An example of a fabrication method and a demonstration of a pH-responsive microcapsule is shown in Fig. 2. Pickering droplets, stabilized with latex particles coated with a responsive polymer, were initially prepared by mechanical emulsification. The latex surface particles were chemically cross-linked to permanently lock the particle film, which serves as a main constructing unit of the colloidal microcapsule. The pH-responsive properties of the coating (pDMAEMA polymer) controlled the porosity of the microcapsule, and the pH-responsive polymer formed an active membrane. The coating molecules expanded away from the latex particle surface upon protonation at low pH and contracted back at high pH due to deprotonation [18]. Interestingly, in this example, not only the release of the encapsulated species could be controlled but also the encapsulation (loading) itself. The colloidal microcapsule did not degrade when it released its content, as in the previous example, but became reswollen. As presented on the right panel of Fig. 2, tuning the swelling degree of a colloidal microcapsule allows retaining the encapsulated species (at high pH values) or loading or releasing the species to/from the microcapsule (at low pH values).

In the aforementioned example of the colloidal microcapsule, the entire shell is composed of the same material (or composite material), and thus the available pores are evenly distributed. This in turn leads to the release of encapsulated material in all different directions through the surface of the capsule. However, if an accurate and efficient targeted release (or loading) is required, such homogenous microcapsules are not the most suitable structures to be used. A targeted, accurate, and directional release is desirable, and recent years have brought progress in this area. Magnetic,

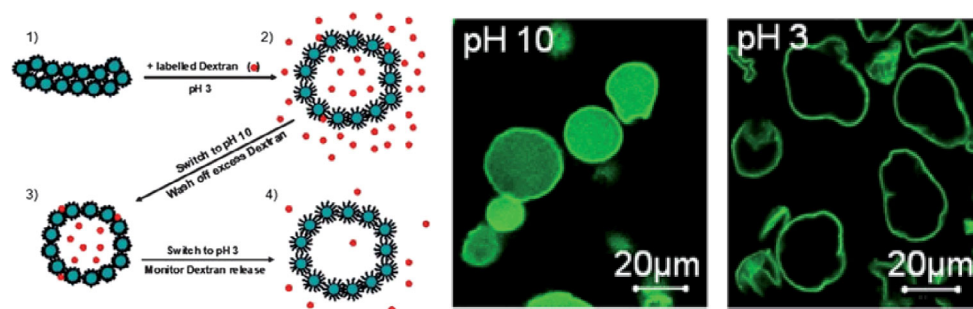


Fig. 2. An example of the loading and releasing mechanism from colloidal capsules. Left: schematic representing conditions for the loading, storage, and subsequent release of the material into/in/from the pH-responsive colloidal microcapsules. The pH-dependent degree of microcapsule swelling is the controlling parameter. In principle, such a colloidal microcapsule can be re-used. Right: fluorescent confocal microscopy images demonstrating that large dextran species can be stored inside the microcapsules for at least 5 h when kept at pH=10 and nearly completely released within 5 h or faster when kept at pH=3. Adapted from [18] with permission from the Royal Society of Chemistry.

decentered core-shell microcapsules are good examples, because the core material can be thermo-triggered and burst-released in a controlled direction [1,51]. In these examples, the direction of release is controlled by an external stimulus. However, if the release has to occur on the target, the target itself has to be localized first (e.g., a target cell inside the body organ) and the above-mentioned microcapsules have no ability to do that; therefore, they are not the most adequate structures of choice. We envision that the patchy colloidal capsule (patchy colloidosome) may contribute to this development. A small patch, a fragment of a shell, can be made of an active material that becomes permeable on-demand, just as in the examples presented in Fig. 2. The patch can be made of a pH-responsive material or any material that changes its permeability in response to some external chemical or physical stimulus. Schematic representations of the release of encapsulated substances from a homogeneous colloidal capsule (left panel) and a patchy colloidal capsule (right panel) are presented as cross-sectional views in Fig. 3. The permeable part of the capsule is represented as red spheres.

Jerri et al. [5] demonstrated a route to engineering anisotropically-functionalized microcapsules. The microcapsule comprised of a polyelectrolyte multilayered spherical shell, which is almost entirely coated by a fused nanoparticle layer serving primarily as a mechanical support (for structure reinforcement). Around 5% of the polyelectrolyte shell surface area is uncoated (patch region), and this is where the core constituents may evacuate from the capsule in a focused manner. The permeability of the patch is controlled by the pH of the solution, and the polyelectrolyte shell swells at low pH values, allowing the encapsulated species to be released from or loaded to the capsule. The fabrication process involves five major steps, which are schematically presented in Fig. 4. After the hollowing step, which is the decomposition and removal of the template core (see Fig. 4(e-f)), the capsule can be loaded by incubating it with different species that are small enough to diffuse through the swollen polyelectrolyte shell (e.g., ionic species).

Higher control and precision in selective targeting and release or loading can be achieved if a part of a capsule (a permeable patch, impermeable shell, or an additional patch) is surface active, which would allow binding the capsule to a desired object. As the concept demonstrator, we will recall the work of Yake et al. [52],

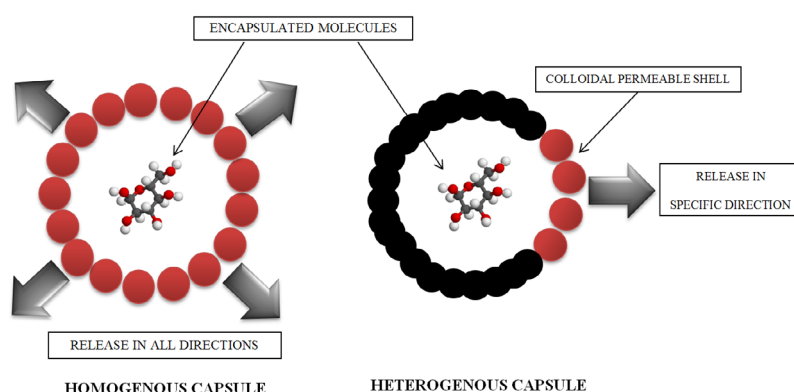


Fig. 3. The release of encapsulated substances from different colloidal capsules: the encapsulated substances are released through the permeable shell. For homogeneous colloidal capsules, the release is in all directions (left). In heterogeneous colloidal capsules (here, one permeable patch), the release is in one specific direction (right). The permeable part of the capsule is represented as red spheres.

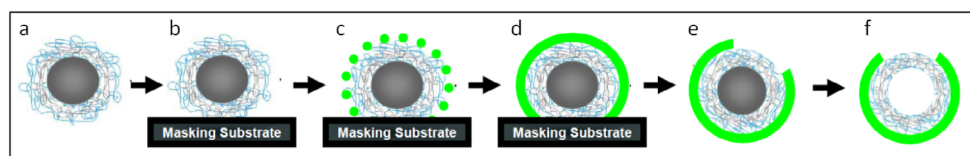


Fig. 4. Process of fabricating stable, dual-functionalized microcapsules. (a) A sacrificial core particle is coated with polyelectrolyte layers in solution, (b) and then settled onto an oppositely-charged masking substrate. (c) The settled particle is selectively coated with nanoparticles. (d) A fusing step bonds the nanoparticles to the underlying polyelectrolyte multilayered particle, forming a barrier shell. (e) The selectively coated particle construction is sonicated off the substrate mask (f) and is then exposed to a HCl solution to decompose the template core, resulting in a hollow lithographed capsule. At this point, the capsule may be loaded by incubating it with a dye or other ionic species. Adapted from [5] with permission from The Royal Society of Chemistry.

which presented a method of synthesizing a patchy microparticle (not a microcapsule) that possesses a multifunctional nanoscale region on its surface—a patch with covalently attached targeting agents (e.g., RGD peptides) that may adhere to the targeted biological cell (e.g., mouse fibroblast cells). Two electron microscopy images in Fig. 5 show how localized targeting to the surface influences the morphology of cytoplasm growth. When patchy microparticles adhere with their peptide-modified patch sites to a biological target cell, a cytoskeleton grows over the particles due to the RGD peptide-activated endocytosis process. The obvious advantage of a microcapsule over a microparticle is that the former may store and release significantly larger amounts of the targeting species. Microcapsules can also be used for material uptake, which would be rather difficult for core particles.

We foresee that even more complex and multifunctional patchy colloidal capsules can be used for a broad range of applications. In Fig. 6 we show examples of colloidal shells produced by utilizing either hydrodynamic liquid flows (Fig. 6(a)), electrohydrodynamic (EHD) flows (Fig. 6(b)), or a mechanism involving a synergetic action of electrohydrodynamic flows and electrocoalescence (Fig. 6(c,d)). These four examples illustrate the conceptual idea and are not yet validated experimentally for

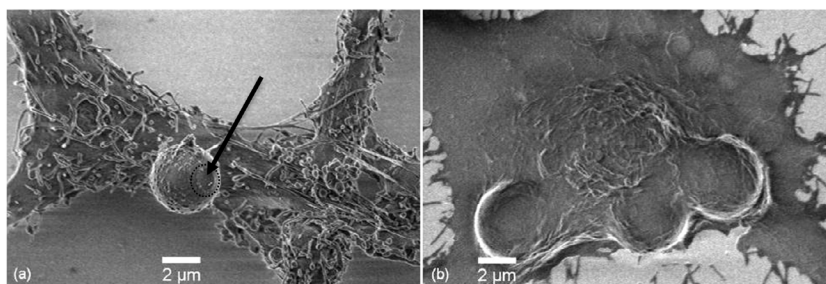


Fig. 5. Localized targeting to the surface influences the morphology of cytoplasm growth: Scanning electron microscopy images of mouse fibroblast cells grown on silicon wafers for 48 hours with inoculated $4\ \mu\text{m}$ patchy particles. (a) A microparticle has nonspecifically adhered to the surface of the cells. The flattened peptide-modified region is indicated by the arrow. (b) Microparticles with peptide-modified patches have specifically adhered to the cell, resulting in the cytoskeleton growth of the cell over the particles due to the RGD peptide-activated endocytosis process. Adapted with permission from [52]. Copyright (2007) American Chemical Society.

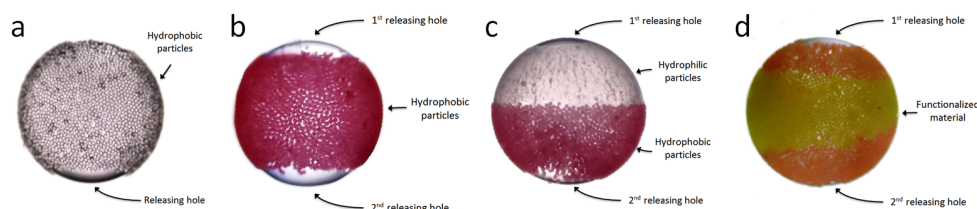


Fig. 6. Four examples of colloidal shells with functional patches: the particle-free regions can be used as releasing holes for material transportation from/to the capsule. Homogenous shells with one (a) or two (b) releasing holes made of polymeric particles. Two types of patchy amphiphilic shell with two particle-free regions (c, d).

usefulness. Each of the shells possesses at least one particle-free region that could be used as a releasing hole. In Fig. 6(a), a homogenous hydrophobic shell is made of densely packed polystyrene (PS) microparticles. The monolayer shell covers nearly the entire surface of the millimetre-sized droplet, with the exception of a small particle-free region on the bottom of the droplet. The shell with one particle-free region can be formed very simply either by the hydrodynamic liquid flows near the droplet surface that drag and arrange the surface particles or by surface-particle sedimentation. The hydrodynamic flows can be induced when a droplet sediments due to the density mismatch between a droplet (e.g., silicone oil with a density of $0.97\ \text{g/cm}^3$) and the dispersing phase (e.g., castor oil with a density of $0.95\ \text{g/cm}^3$), and this was the case for the shell presented in Fig. 6(a). In Fig. 6(b) a homogenous hydrophobic shell is made of densely packed polyethylene (PE) particles with red fluorescent dye. The shell with two particle-free regions was formed by electrohydrodynamic liquid flows (for details see [37]). An example of an amphiphilic Janus-type shell is presented in Fig. 6(c). The grey part of the shell comprises hydrophilic particles (e.g., clay particles), whereas the red part of the shell comprises hydrophobic particles (e.g., polymeric particles). This is an example of a typical amphiphilic structure. In the last example (Fig. 6(d)), the middle part of the shell is made of different material than the rest of the capsules, which in principle would provide an additional functionality;

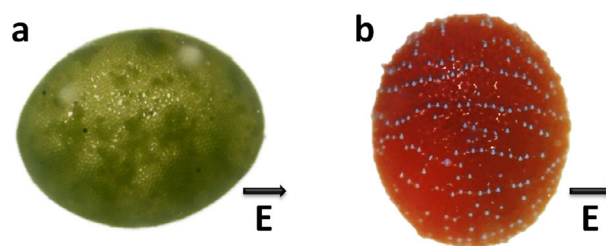


Fig. 7. Electric-field-alignment of colloidal capsules: in the presence of an external electric field, a non-spherical colloidal capsule, comprising dielectrically homogenous spherical microparticles, aligns with its longest axis along the electric field direction (a). A similar non-spherical capsule with conductive chains embedded in the shell aligns with the dipolar chains oriented roughly along the electric field lines, and with the longest geometrical axis normal to the electric field direction (b). The direction of the electric field is indicated by the black arrow.

for example, if the particles had magnetic properties, the orientation of the capsule could be controlled by an external magnetic field.

3 Electro-orientation, magneto-orientation

Induced-orientating of capsules can be realized by applying an external electric or magnetic field. In the presence of an external field, a capsule may undergo orientation due to the induced electric torque. The magnitude of the electric torque is related to the strength of the electric or magnetic dipoles, which are either induced or permanent. The electro-orientation of capsules with induced electric dipoles was demonstrated in our previous work [38]. For a nonspherical colloidal capsule comprising dielectrically homogenous nonconductive particles, such as polyethylene spherical particles, the induced dipole moment aligns along its longest axis (see Fig. 7(a)). This, in turn, determines the alignment of the capsule in the electric field via electro-rotation. Fig. 7(b) shows a non-spherical patchy colloidal capsule comprising both nonconductive (polyethylene) and conductive (silver-coated glass) particles within a monolayer shell. The capsule was made by electrocoalescing of two droplets and by “electro-shaking” (see [53]), allowing the conductive particles to move on the surface of a coalesced droplet and eventually assemble themselves into chains. In the presence of an external electric field, the capsule undergoes electro-orientation and aligns itself with the dipolar chains oriented roughly along the electric field lines. Here the alignment is different from that of the homogenous capsule: the capsule does not align with its longest geometrical axis along the electric field lines, but rather the conductive chains define the direction of alignment. The rotation dynamics is primarily dependent on the viscosity of the surrounding medium and square of the electric field strength. In sum, if the middle part of the shell in Fig. 6(d) is made of material with greatly different dielectric properties than the rest of the shell, the alignment of the capsule will be as in Fig. 6(d) if the electric field is in a horizontal direction.

Sander and co-workers [35] prepared magnetically responsive Janus colloidosomes that could orient under the application of an external magnetic field (Fig. 8). The Janus colloidosomes were prepared using a double emulsification technique in a microfluidic device. The last step of the preparation method involved removing the oil phase; during this stage, a magnet was kept next to the emulsion vial, forming

colloidosomes with uneven particle distribution in the shell. Under rotating magnetic fields, these colloidosomes underwent controlled oscillatory motion, as demonstrated in Fig. 8(a,b). The Janus capsules could also be formed by phase separation due to the dewetting phenomenon, and the resulting capsules are presented in Fig. 8(c).

4 Synthesis of patchy colloidosomes

There are many well-established physical and chemical methods for fabricating homogenous colloidosomes, including membrane or microfluidic emulsification [54], emulsification by mechanical stirring [23], layer-by-layer assembly [55,56], pan coating, spray drying [48], phase separation [57], and more. However, not many methods have been developed yet for synthesizing heterogeneous colloidal capsules. In this section we will present a few example methods for fabricating different patchy colloidosomes.

Subramaniam et al. [36] were one of the first to fabricate Janus colloidal microcapsules. They used a microfluidic chip, designed as a three-channel hydrodynamic focusing device. Differentially labelled with rhodamine and fluorescein, polystyrene microparticles were initially loaded into two outer channels. The particles were then transported towards the focusing channel, where they were adsorbed onto the interface of the dispersing liquid (or gas) and the dispersed liquid. Next, the flow carried the particles to the anterior of the curved interface, which eventually broke and formed a sphere with jammed particles. If the concentrations of particles arriving from each of the outer channels are similar, a Janus-type colloidosome is formed, as shown in Fig. 9. The geometry of the outlet channel and the ratio of particle concentration in one channel to particle concentration in the other channel are the main determinants of both capsule and patch size.

In our recent research, we used a microfluidic chip with two separate flow-focusing junctions to create initial droplets with different microparticles (polymeric particles with different colour dyes; see Fig. 10). The droplets flow through short zigzag-shaped channels where the bulk particles are transported towards the surface of the droplet because of the induced asymmetric hydrodynamic flows inside and outside the droplet. Next, the droplets are carried towards the main reservoir with two long electrodes placed parallel between the channels. The Janus capsules are formed by the synergistic action of electrohydrodynamic (EDH) flows and electrocoalescence (explained in greater detail farther down). Under application of an external electric field, electric dipoles were induced and droplets started to move towards one another. At the same time, colloidal particles were transported away from the electric poles of the droplets, which enabled the electrocoalescence of the droplets. After a couple of seconds, the droplets merged and the Janus colloidal capsule was formed, as illustrated in Fig. 11.

The shape of a jammed shell is determined by the concentration of surface particles. Above a certain particle concentration (see Supplementary Information), arrested nonspherical capsules are formed, and if the concentration is too low, a stable shell cannot be formed because the surface particles are not jammed. The challenge is to control particle concentration and stability at the interface. The binding energy of a particle at the interface is related to both the particle size and the contact angle. If a particle possesses a too large affinity for either phase, the contact angle deviates from the optimal angle of 90° , and even gentle deformation or displacement of the droplet causes the particles to detach from the surface. Figure 12 shows silicone oil microdroplets with polystyrene (top) and polyethylene (bottom) particles. The polystyrene particles have a much higher affinity to the dispersing phase (castor oil) than to the silicone oil droplet, and they therefore reside in the channel.

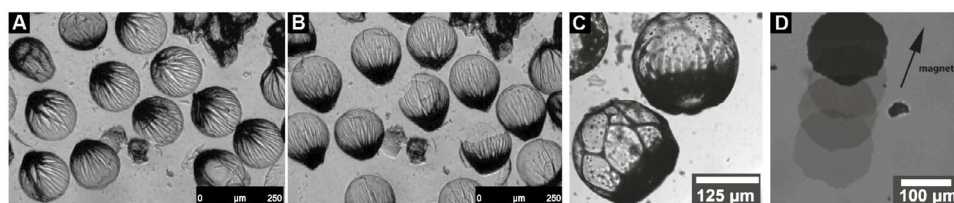


Fig. 8. Magnetically responsive Janus colloidal capsules able to orient and move in magnetic fields: Silanized $\text{SiO}_2\text{-Fe}_3\text{O}_4$ patchy colloidosomes made by applying a magnetic field during oil removal. The patchy capsules undergo controlled oscillatory motion by applying rotating magnetic fields (a, b). Janus magnetic colloidosomes obtained by phase separation induced during the dewetting (c). Motion of an $\text{Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ composite colloidosome in response to a magnetic field gradient (d). Adapted with permission from [35]. Copyright (2011) American Chemical Society.

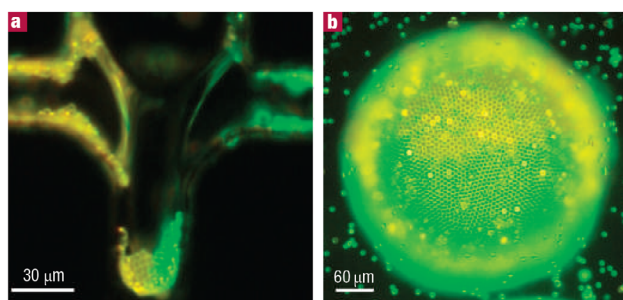


Fig. 9. Janus colloidal capsule produced by means of microfluidics: Assembly of particles on an air–water interface. Particles with a diameter of around $5\ \mu\text{m}$ are dyed yellow and green with rhodamine and fluorescein (a). An example of the Janus capsule, with approximately two hemispheres of different size particles and fluorescence. Reprinted by permission from Macmillan Publishers Ltd: [Nature Materials] [36], copyright (2005).

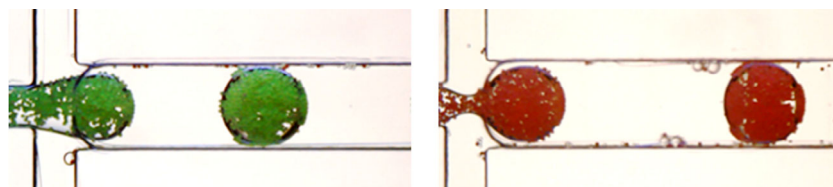


Fig. 10. Formation of initial droplets: Initial droplets with both the surface and the bulk particles are formed in two separate flow-focusing junctions. The right concentration of particles is required to create the final jammed colloidal shell on an electrocoalesced droplet.

It is possible to chemically modify the surface of the particles, which may help to balance the wettability of the particles by the liquids. In our previous experiments, we used an acrylate polymer surface modifier to improve the affinity of polystyrene particles towards castor oil. The modification changed the contact angle (compare Fig. 13(a) with Fig. 13(b)), and the particles held more strongly to the interface, as shown in Fig. 13(b) and Fig. 13(d). Another way to ensure particle stability would be to use heterogonous colloidal particles (e.g., Janus particles) in which two hemispheres are composed of different materials that possess the right affinity to both liquid phases. The equilibrium contact angle for such particles is nearly 90° [17]. Yang et al. recently fabricated a colloidosome composed of Janus particles [58]. (Comment: The researchers named the structure a *Janus colloidosome* because the wettability of the

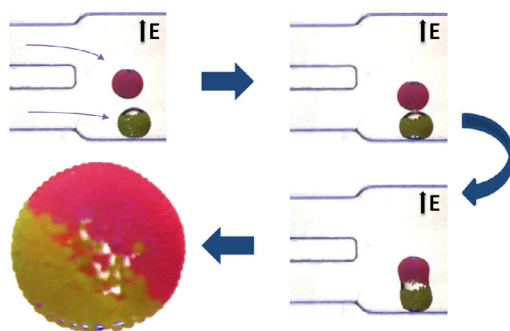


Fig. 11. Fabrication of Janus colloidal capsules in a microfluidic device by means of electric fields. Two droplets with polymeric particles (with red and green dyes) have just left the small channels and entered the reservoir. An electric field is applied in a vertical direction. Due to EDH flows the particles move away from the electric poles of the droplets. The droplets attract one another and finally coalesce, resulting in Janus capsule formation.

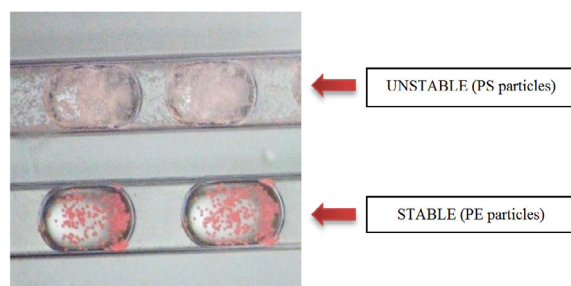


Fig. 12. Importance of the stability of particles at the interface: PS particles do not hold on the surface of a droplet. Many of the PS particles reside in the continuous phase (top). PE particles bind more strongly to the interface (bottom).

colloidal capsule's exterior surface is different from that of the interior surface. In our opinion, this is not adequate terminology. *Janus* commonly refers to objects whose surface (outer layer) has two distinct properties, such as particles, vesicles, and polymersomes. Thus, what Yang et al. [58] presented is a *colloidosome* made of Janus colloidal particles.)

Another route for fabricating patchy colloidal capsules was presented in our previous work, in which the capsules were made on the surfaces of silicone oil droplets by synergetic action of electrohydrodynamic flows and electrocoalescence [37]. The electrohydrodynamic flows were used to guide-assemble surface particles. Figure 14(a) shows the flow patterns obtained by tracing a few particles located outside the droplet. The surface particles were carried towards the electric equator of the droplet, as shown in Fig. 14(b). That in turn cleared up the two areas on the electric poles and consequently enabled electrocoalescence.

Figure 15(a) shows the initial droplets partially covered by surface particles assembled at electric equators by EHD flows. The droplets attract one another by means of both the EHD flows and electrostatic interaction, i.e., dielectrophoresis due to the induced electric dipoles. The droplets electro-coalesce soon after they come into physical contact, and the Janus colloidal shell can be formed on the surface of the electrocoalesced droplet, as shown in Fig. 15(b) (see also Supplementary Movie 1).

By adequately choosing both the particle concentration and the size of each droplet, either spherical or nonspherical capsules can be made with different

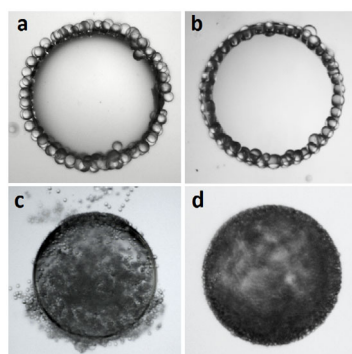


Fig. 13. Chemical modification of particles to improve the binding of particles to the interface: A silicone oil with pure (a, c) and surface-modified (b, d) PS particles with radii of 140 and 40 μm in panels (a, b) and (c, d), respectively. The droplets are immersed in castor oil. The pure PS particles are weakly bound to the interface. Gentle deformation or displacement of the droplet caused the nonmodified particles to easily detach from the surface and diffuse to the castor oil phase to which they have greater affinity (c). The surface modification of PS particles change the contact angle, and the modified PS particles bind strongly to the interface (d). In (a) and (b), particles are assembled at the electric equator of a droplet by the EHD flows, and the images are taken along the electric field lines. Reprinted with permission from [38].

material share. Examples of patchy capsules are shown in Fig. 16, and these include a spherical, an oval, a dumbbell-like, a double-ball, and a bulb-like capsule, Fig. 16(a) to Fig. 16(e), respectively. The patchy colloidal capsules were composed of hydrophobic polyethylene (red and green) and hydrophilic clay mineral particles (grey). The clay and polyethylene particles differ by size and dielectric properties.

The particles that form the patchy colloidal capsules presented in Fig. 16 have not been permanently locked (sintered or fused by any means). However, we observe that micron- and sub-micron-sized particles can form stable structures of different shapes, and these shapes also remain stable when the electric field is turned off. The heterogeneous Pickering layer of such patchy colloidal capsules is composed of jammed particles and resembles a Bingham plastic – that is, a viscoplastic material – that behaves as a rigid body at low stresses but flows at high stresses. The capsule remains stable as long as an applied stress (induced internally by, for example, mechanical shearing or externally by electric fields) imposed on the capsule is low and its magnitude is smaller than the deformation yield point of the Pickering layer. Otherwise, the capsule may undergo an irreversible shape transition. We expect that the deformation mechanisms of patchy colloidal capsules or the cracking and crack propagation mechanisms of patchy colloidosomes can be more complex than those of a homogenous colloidal capsule or colloidosomes.

5 Self-propulsion and motility of patchy colloidosomes

A very interesting research aspect is the motility of patchy colloidosomes. To execute a nonequilibrium activity such as motility, a microcapsule needs to acquire free energy. The energy can be provided externally through applying an electric or magnetic field, light illumination, and so on, or internally when a flow field (necessary for inducing motion) is generated either by the capsule itself or a neighbouring object. The motion of a capsule or a collection of capsules can be induced via different mechanisms. Typical examples include the electrophoretic motion of a charged object, dielectrophoretic

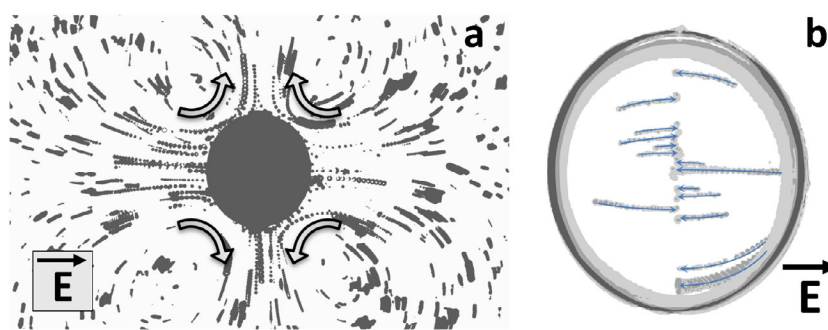


Fig. 14. EHD flows and particle assembly at the electric equator: experimentally observed hydrodynamic streamlines outside the droplet (a) and on the surface of the droplet (b). The arrows indicate the direction of movement of several tracer particles. The size of each droplet is about 3 mm. An electric field of 200 Vmm^{-1} is applied in the horizontal direction. Reprinted with permission from [38].

motion in the presence of an electric field gradient [59], magnetophoretic motion in the presence of a magnetic field gradient [60] (an example is shown in Fig. 8(d)), contact charge electrophoresis (charge acquired by contact with an electrode) [61], and so on. As interest grows in the field of science related to patchy structures, different mechanisms for the single or collective motion of patchy structures have been recognized. Owing to the symmetrical breaking of a patchy structure (e.g., a patch is made of material dielectrically different from the rest of the shell), electrophoretic motion may occur despite the intrinsically uncharged patchy structure (see Fig. 17(a)). This is due to the asymmetric hydrodynamic flows of liquids (induced by an external electric field) that exert a directional force on the patchy structure. For greater detail regarding the induced-charge electrophoresis of heterogeneous structures, see the theoretical considerations by Squires and Bazant [62,63]. A thermally inhomogeneous patchy structure may experience the self-propulsion due to the thermophoresis. An excess temperature can be induced on a patchy region and form a local temperature gradient, e.g., if the patchy structure is heated by a magnetic field [64] or illuminated with a laser light [65–67]. Figure 17(b) shows a sketch of a Janus structure comprised of shells with different light adsorption coefficients. Propulsion can also be provided by chemical reactions, such as the asymmetric distribution of reaction products [68]. A schematic representation of an enzymatic-driven propulsion is shown in Fig. 17(c). We believe that a simple motion of a patchy colloidosome or a motion due to the collective effects will be an interesting and fruitful area of the related research.

6 Summary and perspectives

At present, the large-scale fabrication of colloidal capsules remains a challenge, especially when considering multi-patchy and multi-functional colloidosomes. The above-mentioned patchy colloidal capsules were prepared by either mechanical pipetting or microfluidic means. The former approach allows for fabricating one patchy capsule at the time, and it is used to demonstrate a proof of concept that needs further development. The individually produced patchy capsules may still be very convenient for further fundamental research related to the mechanical properties of such anisotropic capsules and instabilities of patchy Pickering films; for example, the mechanisms of adsorption of the external stress are imposed on a capsule by applying an

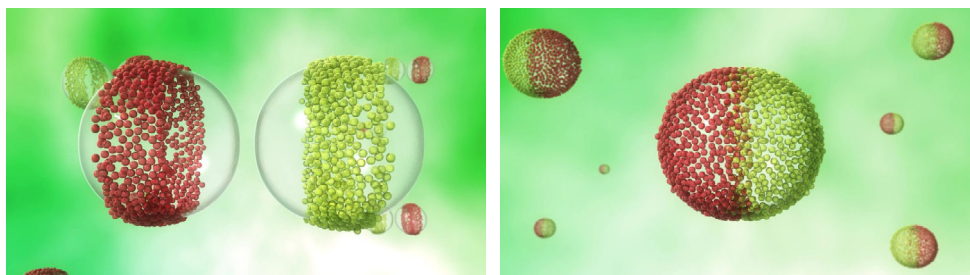


Fig. 15. Janus colloidal capsule made by electro-coalescence with the assistance of EHD flows [45] (visualization): The initial droplets partially covered by surface particles assembled at electric equators by EHD flows (a). The droplets attract one another by means of both the EHD flows and electrostatic interaction. The droplets electro-coalesce soon after they come into physical contact and the Janus shell is formed on the surface of the electrocoalesced droplet (see also Supplementary Movie 1).

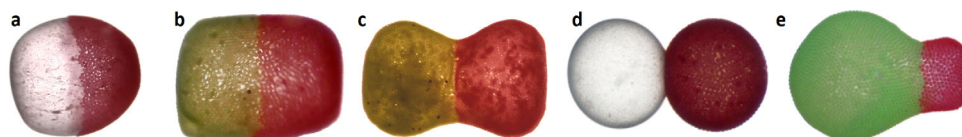


Fig. 16. Examples of patchy colloidal capsules fabricated by means of EHD flows and electro-coalescence: A spherical, an oval, a dumbbell-like, a double-ball and a bulb-like capsule, from (a) to (e), respectively.

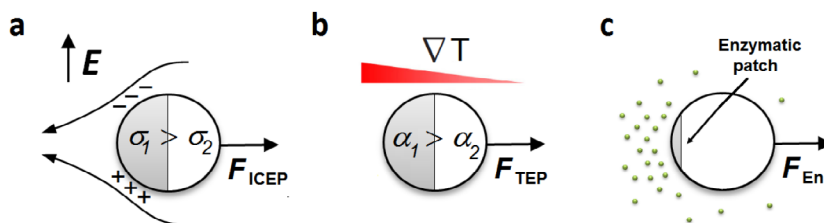


Fig. 17. Different mechanisms of motion: A sketch showing a mechanism of propulsion by induced-charge electrophoresis (a), induced thermo-phoresis (b), and via enzymatic reaction converting chemical energy to mechanical work (c).

external electric field. We envision that the mechanism of complex capsule deformation (e.g., crumpling, elastic deformation, viscoelastic relaxation, shell unjamming, solid-to-liquid transition, etc.) is different than that of a homogenous capsule. The electric-field-induced deformation of capsules (e.g., by compression or elongation) will most likely depend on shell particle electric properties, geometry (e.g., spherical vs disc-shaped), packing density, and so on. The microfluidic approach yields a higher production rate but is still not high enough for mass-producing Pickering emulsions with patchy colloidosomes. We look forward with enthusiasm to further developments in the subject of patchy colloidosomes and other artificial patchy vesicles, such as patchy polymersomes [40, 43].

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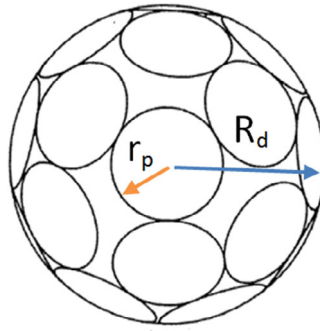


Fig. S1. A schematic drawing of circles occupying surface of a sphere: A possible packing of 19 circles on a surface of a sphere, with marked radius of droplet and particle. Adapted from [68] with permission from Springer.

Supplementary information

The concentration of particles measured by mass that needs to be used to occupy entire surface of one droplet of a specific radius:

$$\frac{m_p}{m_d} = 4 \cdot \phi \cdot \frac{\rho_p \cdot r_p}{\rho_d \cdot R_d}$$

where: ρ_p , ρ_d , r_p , R_d are densities and radii of particle and droplet, respectively; and ϕ is the packing density factor. Packing density of circles on a sphere is generally a function of number of the circles. For an infinite number of circles, the packing density approaches 0.906, i.e., achieve the same optimal packing density as for circles forming hexagonal pattern on a 2-D plane. Since we assume here that $R_d \gg r_p$, the packing density ϕ can be assigned as approximately 0.9.

For example, $\frac{m_p}{m_d} [\%] = 10\%$ if $\rho_p = 1.05 \text{ g/cm}^3$; $\rho_p = 0.95 \text{ g/cm}^3$, $r_d = 400 \mu\text{m}$.

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